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Localized spin wave modes in an isotropic Heisenberg ferromagnet in presence of biquadratic exchange

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This paper discusses the appearance of localized spin wave modes in an isotropic Heisenberg ferromagnet in presence of a single substitutional impurity. The atomic spins are assumed to be coupled by bilinear and biquadratic exchange interactions. The double-time temperature-dependent Green's function formalism is used with proper decoupling. The five-spin Green's functions appearing in the biquadratic part of the equation of motion are decoupled by using the random phase approximation and the scheme of Anderson and Callen, while the Green's functions in the bilinear part have been decoupled by PRA. Equations are solved to give the localized modes depending on the biquadratic parameter α in an interesting way. It is seen that the effect of the biquadratic exchange on the localized modes necessarily depends on the sign of α. If it be positive, a mode feels harder to split off the spin wave band, but if it is negative, a mode feels easier to split off. The validity of these results has been studied with reference to some resonance measurements in $KMnF_3 : Ni^{++}$ and $Fe : Mn^{++}$. A sign-rule for α has also been constructed from a comparison between the theoretical and experimental results. Finally, some predictions have been made regarding the situations related to the appearance of localized modes in $KNiF_4 : Mn^{++}$.

1 Introduction

The appearance of localized spin wave modes in impure Heisenberg systems first pointed out independently by Wolfram & Callaway (1963) and by Takeno (1963) has been subsequently studied with gradually increasing sophistications by several authors using several different methods (Hone & Callen 1963, Hone *et al* 1963, Ishii *et al* (1965, Izyumov & Medvedev 1965, Tonegawa & Kanamori 1966, Wang & Callen 1967, Livesey 1968, Watarai & Kawasaki 1972, Tanaka *et al* 1973, 1974). It is to be observed that all these observations were performed on the basis of the fundamental Hamiltonian which is bilinear in spin variables. That is, the host-host interaction or the host-impurity interaction were represented by usual bilinear type exchange integrals. But the use of bilinear exchange only has been found to be insufficient in explaining some resonance measurements and for proper interpretation of facts the existence of a biquadratic exchange was felt to be indispensable (Harris & Owen 1963, Rodbell *et al* 1964, Joseph 1965). Some theoretical works regarding the effect of the biquadratic exchange on various statistical-mechanical properties of the magnetic systems have been

carried out (Brown 1971, Nauciel-Bloch *et al* 1972, Chakraborty 1974, 1976) It may, therefore, be expected that the consideration of biquadratic exchange will also modify the localized spin wave modes in an important way

The purpose of the present paper is to discuss, within the Green's function framework, the effects of biquadratic exchange on the localized spin waves modes in an isotropic Heisenberg ferromagnet The equations are decoupled in lowest order, but taking some account of spin correlations. Expression for localized modes is then derived, which shows that a positive biquadratic exchange, in certain cases, hinders the formation of a localized mode, while a negative biquadratic exchange enhances the possibility of formation a localized modes The consistency of this result is then critically examined in the light of the situations occurring in the case of formation of localized modes in $KMnF_3$ and in Fe doped by impurities Ni^{++} and M_n^{++} respectively. A sign-rule for α for a magnetic system is found to be necessary and is constructed by studying the theoretical magnetization curves of Brown (1971) and the experimental magnetization curves obtained by several authors from resonance measurements The role of the biquadratic parameter in enhancing and hindering the formation of localized modes is demonstrated graphically for a spin-1 lattice

In Sec 7 the results of the present calculation have been applied to the sample $KNiF_3$ doped by impurities Mn^{++}, and some predictions have been made regarding the appearance of localized modes It is concluded that the localized modes will appear at high temperature in $KNiF_3 \cdot M_n^{++}$ An approximate estimate of this temperature has been made

2 Basic Hamiltonian and the Equation of Motion

Let us consider a system of spins coupled by the bilinear and biquadratic exchange interactions and let us assume that a single impurity of spin S_I is situated at the lattice site c The exchange interactions between the host spins at sites i and j are denoted by $2J_{ij}$ and $2J'_{ij}$, the former being bilinear type and the latter biquadratic type Let the host-impurity interactions be represented by $2(J_{ic}+I_{ic})$ and $2(J'_{ic}+I'_{ic})$. Our first simplifying assumptions are $I_{ic}=0$ and $I'_{ic}=0$ These assumptions will simplify the problem considerably without affecting the general qualitative results

The Hamiltonian of the system may, therefore, be represented by the following simple form

$$H = -\sum_{<ij>} J_{ij}(\boldsymbol{S}_i \cdot \boldsymbol{S}_j) - \sum_{<ij>} J'_{ij}(\boldsymbol{S}_i \cdot \boldsymbol{S}_j)^2 \qquad \ldots (1)$$

where the summation runs over all pairs of neighbours i and j. The impurity spin situated at the lattice site c is assumed to be included in the index i or j.

that is, it has substituted one host spin at the lattice site c. The second term corresponds to the biquadratic interaction.

Let us now employ the two-time temperature-dependent Green's function $G_{gm}(t)$ defined in the form

$$G_{gm}(t) = \ll S_g^+ ; S_m^- \gg = -i\theta(t) \langle [S_g^+(t), S_m^-(0)] \rangle \tag{2}$$

where the square bracket denotes a commutator, angular brackets denote the ensemble averages, and $\theta(t)$ is a step function which is equal to unity for $t > 0$ and zero for $t > 0$. The symbols g and f refer to the lattice sites.

Equation of motion for the Green's function can be derived by using the Hamiltonian (1) and the usual commutation relations for spin operators. The equation of motion for $G_{gm}(E)$ which is the Fourier-transform of $G_{gm}(t)$ may be shown to be

$$\begin{aligned} E\, G_{gm}(t) = {} & \frac{1}{\pi} \langle S_{gz} \rangle \delta_{gm} + 2 \sum_f J_{gf} \ll (S_f^z S_g^+ - S_g^z S_f^+); S_m^- \gg \\ & + 2 \sum_f J'_{gf} \ll [(S_f^z)^2 (S_g^z S_g^+ + S_g^+ S_{gz}) - (S_g^z)^2 (S_f^z S_f^+ + S_f^+ S_f^z) \\ & + \tfrac{1}{2}(S_f^z S_f^- + S_f^- S_f^z) S_g^+ S_g^+ - \tfrac{1}{2}(S_g^z S_g + S_g^- S_g^z) S_f^+ S_f^+ \\ & + \tfrac{1}{2}(S_f^z S_f^+ S_g^+ S_g^- + S_f^+ S_f^z S_g^- S_g^+) \\ & - \tfrac{1}{2}(S_g^z S_g^+ S_f^+ S_f^- + S_g^+ S_g^z S_f^- S_f^+)], S_m^- \gg, \quad f \neq g \end{aligned} \tag{3}$$

Eq. (3) is apparently similar in form with that obtained for a pure ferromagnet with both bilinear and biquadratic exchange interactions. There is, however, much difference in two forms. In eq (3) the impurity site c is included in the index g or f, and consequently the magnetization at site c may differ appreciably from that at any other site in the crystal. In a pure ferromagnet the magnetization cannot differ much from one lattice site to another lattice site provided the groundstate is assumed to be ferromagnetic. In presence of biquadratic exchange it may happen, in certain circumstances, that the groundstate of the system does not become ferromagnetic. Such situation may occur when the biquadratic exchange is much negative so that the bilinear part becomes less predominant and in such case the antiferromagnetic spin configuration becomes favourable. The quantum condition for a ferromagnetic groundstate has been derived by Nauciel-Bloch *et al* (1972) which is

$$-5 < j/J < 1$$

where J and j are nearest-neighbour bilinear and biquadratic exchange constants respectively. Author has shown (Chakraborty 1976) that throughout this whole range of values of biquadratic parameter $\alpha = j/J$ no quadrupolar phase can come to occur. Our fundamental assumption is, therefore, that the ground state of the system described by the Hamiltonian is ferromagnetic and the magnitude of the biquadratic exchange lies within the range stated above.

We now turn our attention to the difficulty aasociated with the adequate solution of the equation of motion for the Green's function The major difficulty related to eq (3) is that the hierarchy of Green s functions contained in it practically renders the problem unsolvable There exist, however, approximate methods of solving such problems in so-called truncation processes, which decouple the equations to form a closed set that can be solved for two-spin Green's functions The Fourier-transform of these Green's functions are related to corresponding temperature-dependent correlation functions which dete mine the thermodynamic properties of the system In the present context, we restrict ourselves to finding out the conditions for the existence of localized spin wave modes in different possible situations and so the first necessary task is the termination of the hen archy of the Green's functions by means of adequate decoupling approximations

3 Decoupling Approximntions and the Linearization of Equation of Motion

The Green s functions which occur in the bilmear part of the equation of motion are usual three-spin Green's functions We employ the random phase approximation (RPA) for decoupling these Green's functions

$$S_f S_g{}^+ ; S_m{}^- \gg_{f\neq g} = \quad S_f{}^z \cdot \ll S_g{}^+ \ S_m{}^- \gg \qquad . \quad (4)$$

It is to be noted that $< S_f{}^z >$ has not been replaced by $< S^z >$ because the magnetization at the impurity site may differ appreciably from that at the host site

The Green's functions which appear in the biquadratic part of the equation of motion are five-spin Green's functions and these Green's functions evidently create a lot of troubles in solving the problem We decouple these Green's functions in two successive steps The first one is the utilization of RPA which reduces the five-spin Green's functions to three-spin Green's functions

$$\ll (S_f{}^z)^2 (S_g{}^z S_g{}^- + S_g{}^+ S_g{}^z),\ S_m{}^- \gg_{f\neq g} = < (S_f{}^z)^2 > \ \ll (S_g{}^z S_g{}^+ + S_g{}^+ S_g{}^z) \cdot \ S_m{}^- \gg , \quad . . \quad (5)$$

$$\ll S_g{}^+ S_g{}^- (S_f{}^z \ S_f \ + S_f{}^- S_f{}^z),\ S_m{}^- \gg_{f\neq g} = < \ S_g{}^+ S_g{}^- > \ll (S_f{}^z S_f{}^- + S_f{}^- S_f{}^z) : S_m{}^- \gg , \quad . . \quad (6)$$

$$\ll S_f{}^- S_f{}^+ S_g{}^z S_g{}^+ .\ S_m{}^- \gg_{f\neq g} = < \ S_f{}^- S_f{}^+ > \ll S_g{}^z S_g{}^+ ,\ S_m{}^- \gg \qquad (7)$$

The correlation function $< S_g{}^+ S_g{}^+ >$ disappears because the product $S_g{}^+ S_g{}^+$ is not diagonal in the total z-component of spin It is necessary to remark that in writing out the eqs (5), (6) and (7) we have ignored the correlation between the spins at different sites It is, indeed, impossible to assess the exact magnitude of spin-correlation in these cases

At this stage the equation of motion reduces to the form

$$EG_{gm}(E) = (<S_g^z>/\pi)\delta_{gm} + 2\sum_f J_{gf}[<S_f^z> G_{gm}(E) - <S_g^z> G_{fm}(E)]$$

$$+2\sum_f J'_{gf}[F_f \ll (S_g^z S_g^+ + S_g^+ S_g^z) \quad S_m^- \gg - F_g \ll (S_g^z S_f^+ + S_f^+ S_f^z);\ S_m^- \gg$$

$$+ <S_g^z> \ll S_f^z S_f^+ .\ S_m^- \gg - <S_f^z> \ll S_g^z S_g^+ .\ S_m^- \gg] \quad \ldots \quad 8)$$

where the symbol F_f is given by

$$F_f = <(S_f^z)^2> - \tfrac{1}{2} < S_f \ S_f^+ > \quad \ldots \quad (9)$$

The Green's functions which is now to be decoupled are three-spin Green's function of the special form $\ll S_g^z S_g^+ .\ S_m^- \gg$ Such type of Green's function has already occurred in the wellknown problem of single-ion crystal-field anisotropy It is very difficult to decouple this Green's function by any conventional decoupling scheme such as RPA In this connection it is worth mentioning that several different decoupling schemes were devised to overcome the difficulty in solving the problem Narath (1965) utilized a decoupling scheme which is, in fact, an inappropriate representation of RPA and has been severaly criticized by subsequent authors Lines (1967) made use of a decoupling scheme which is only applicable in the problem of single-ion anisotropy and cannot be applied to other problem such as that of biquadratic exchange Moreover, his scheme also suffers from the drawback that a theorem of Callen and Strikeman was to be applied for getting the resulting magnetization, and the Callen and Strikeman's theorem is only valid for small single-ion anisotropy In an altogether different approach, Murao & Matsubara (1968) were able to treate the problem quite satisfactorily, but their approach is specially designed for decoupling the single-ion terms and so it is very difficult to employ their approach in the present problem A simple and general way of decoupling such Green's function was adopted by Anderson & Callen (1964) although on the basis of several heuristic reasonings Because of its simplicity and its applicability within a wide range of temperatures (Lines 1967) we employ this scheme in the present problem The scheme of Anderson and Gallen may be stated in the form

$$\ll (S_g^z S_g^+ + S_g^+ S_g^z);\ S_m \gg$$
$$= <S_g^z>[2 - P_g(<S_g^- S_g^+> + <S_g^+ S_g^->)] \ll S_g^+ ,\ S_m^- \gg \quad . \quad (10)$$

where P_g is a parameter which is to be chosen to satisfy the kinematical constraints In RPA, $P_g = 0$ Following Anderson and Callen we assume

$$P_g = \frac{1}{2S^2} \qquad \text{for } g \neq c$$

$$= \frac{1}{2S_I^2} \qquad \text{for } g = c \quad \ldots \quad (11)$$

where S and S_I are the host-spin and the impurity spin respectively It is to be noticed that in the decoupling (10) we have written $<S_g{}^z>$ in place of $<S^z>$ as used by Anderson & Callen (1964)

Employing the decoupling procedure discussed above and utilizing the following fundamental identities

$$<S_g{}^+ S_g{}^-> = S(S+1) - <(S_g{}^z)^2> + <S_g{}^z>$$
$$<S_g{}^- S_g{}^+> = S(S+1) - <(S_g{}^z)^2> - <S_g{}^z> \quad .. \quad (12)$$

one obtains the equation of motion in the form

$$E G_{gm}(E) = \frac{<S_g{}^z>}{\pi} \delta_{gm} + 2 \sum_f [(J_{gf} - \tfrac{1}{2} J'_{gf}) < S_f{}^z > G_{gm}(E)$$

$$+ \frac{3}{2S_g{}^2} B_f < S_g{}^z > J'_{gf} \{2S_g{}^2 + B_g - \tfrac{2}{3} S(S+1)\}] G_{gm}(E)$$

$$- 2 \sum_f [(J_{gf} - \tfrac{1}{2} J'_{gf}) < S_g{}^z >$$

$$+ \frac{3}{2S_f{}^2} B_g < S_f{}^z > J'_{gf} \{2S_f{}^2 + B_f - \tfrac{2}{3} S(S+1)\}] G_{fm}(E) \qquad (13)$$

where the symbol B stands for the expression

$$B_f = <(S_f{}^z)^2> - \tfrac{1}{3} S(S+1) \quad .. \quad (14)$$

It is to be remarked that when the following equalities are satisfied

$$<S_f{}^z> = <S_g{}^z> = <S^z>. \quad <(S_f{}^z)^2> = <(S_g{}^z)^2> = <(S^z)^2>$$

one will get $B_f = B_g = B$ and such a parameter will then be called a ***quadrupolar*** parameter which is responsible for a separate phase transition (Nauciel-Bloch *et al*, 1972, Chakraborty 1976) In the present problem it should be noted that due to the presence of the impurity it is not possible to introduce a single quadrupolar parameter This complicates the problem to a large extent. We, therefore, assume that the quadrupolar parameter for the corresponding pure system is zero which is equivalent to the isotropy assumption for the host lattice The same assumption is obviously meaningless for the impurity spin

4 Localized Spin Wave Modes

The linearized equation of motion derived in the previous section can be employed to discuss the effect of biquadratic exchange on the localized spin

wave modes in a very simple way by introducing the *polarization-level-deviation* parameter d_f defined by

$$d_f = L_f - 1,$$

where $L_f = \langle S_f^z \rangle / \langle S^z \rangle$ is the polarization level of the f-th spin, $\langle S^z \rangle$ being the magnetization in the unperturbed lattice. When there is no impurity in the system we have $\langle S^z_f \rangle = \langle S^z \rangle$ and hence $d_f = 0$ which may, therefore, be regarded as the condition for non-occurrence of a localized mode. The localized modes can appear for $d_f \neq 0$ which is the basic condition to be utilized for a discussion of the existence of localized modes. We assume that the perturbation due to the impurity is highly localized so that one has $L_f = 1$ for $f \neq c$ which implies that the magnetization at the impurity site is different from the average host-magnetization. The assumption means that $d_f \neq 0$ for $f = c$ only and zero otherwise.

We write out first the equation of motion in terms of L_f or d_f. But there is a major problem. It is very difficult to write B_f or B_g in terms L or d. Following approximation may resolve the difficulty. By the isotropy assumption for the unperturbed lattice (also since there is no quadrupolar phase) we note that

$$B_f = \langle (S_f^z)^2 \rangle - \tfrac{1}{3} S(S+1) = \langle (S^z_f)^2 \rangle - \langle (S^z)^2 \rangle \quad \ldots (15)$$

Using the approximation

$$\frac{\langle (S_f^z)^2 \rangle}{\langle (S^z)^2 \rangle} \cong L_f^2, \quad (16)$$

one gets B_f in the form

$$B_f = \tfrac{1}{3} S(S+1)(L_f^2 - 1) \quad \ldots (17)$$

We now consider g and f as nearest-neighbours and hence the exchange integrals are to be replaced by exchange constants. Let J and J' be the exchange constants corresponding to the bilinear and biquadratic exchange respectively. Then it is the usual procedure to define a biquadratic parameter $\alpha = J'/J$. Substituting now $g = c$, $m = c$, $f = c'$ and $g = c'$, $m = c$, $f = c$ (where c and c' are nearest neighbours) we get

$$EG_{cc}(E) = -\frac{\langle S_c^z \rangle}{\pi} + 2Z \langle S^z \rangle J \left[(1 - \tfrac{1}{2}\alpha) L_c' + \frac{3}{2S^2} \alpha B_c' L_c A_c \right] G_{cc}(E)$$

$$- 2z \langle S^z \rangle J \left[(1 - \tfrac{1}{2}\alpha) L_c + \frac{3}{2S_1^2} \alpha B_c L_c A_c \right] G_{c'c}(E), \quad \ldots (18)$$

$$EG_{c'c}(E) = 2z \langle S^z \rangle J \left[(1 - \tfrac{1}{2}\alpha) L_c + \frac{3}{2S_1^2} \alpha B_c A_{c'} L_{c'} \right] G_{c'c}(E)$$

$$- 2z \langle S^z \rangle J \left[(1 - \tfrac{1}{2}\alpha) L_{c'} + \frac{3}{2S^2} \alpha B_{c'} A_c L_c \right] G_{cc}(E), \quad \ldots (19)$$

where the symbols A and A_c' are given by the following expressions

$$A_c = 2S_1^2 + B_c - \tfrac{2}{3}S(S+1)$$

$$A_c' = 2S^2 + B_c' - \tfrac{2}{3}S(S+1)$$

Since we have assumed that the effect of perturbation due to the impurity is highly localized at the site c we utilize the condition

$$L_f = 1 \qquad \text{for } f \neq c$$

$$= L_c \qquad \text{for } f = c$$

This condition is exactly consistent with the assumption for B and also with the eq (17) Using this condition in eq (17) we observe that for $f \neq c$, $B_f = 0$ and for $f = c$, $B_f \neq 0$ which was our previous assumption regarding B for pure and impure ferromagnets

Eliminating $G_{c'c}$ from eqs (18) and (19) we now get

$$G_{cc}(E) = \frac{\langle S^z \rangle}{\pi} (1 + d_c) \frac{E - E_0\phi}{E^2 - E_0(1+\phi) + \frac{1}{2}\alpha E_0^2\phi}, \qquad \ldots (21)$$

where ϕ stands for the expression

$$\phi = 1 + L_c(1 + \tfrac{1}{2}\alpha) + \frac{3}{2\langle S^z \rangle} B_c A_c'$$

and $E_0 = 2zJ\langle S^z \rangle$ being the RPA energy spectrum for the pure system

Zeroes of the denominator of eq (21) determine the poles of which will give the localized modes

$$\frac{E_q}{E_0} = \tfrac{1}{2}(1+\phi)\left[1 + \left\{1 - \frac{\alpha\phi}{(1+\phi)^2}\right\}^{\frac{1}{2}}\right] \qquad \ldots (22)$$

The negative sign of the quadratic solution has been disregarded because it leads to unphysical result In this case one will find that for $\alpha = 0$, E_q/E_0 vanishes for all α which must not be the case in reality.

One can draw some significant conclusions from eq (22) These are as follows

(i) For $\alpha = 0$, one finds that a localized mode will split off the spin Wave band if $d_c > 0$ which is the usual condition for the appearance of a localized mode in a Heisenberg ferromagnet described by the bilinear exchange only If $d_c < 0$ no localized mode should be observed However, as the temperature increases, an excitation may split off the band at finite temperature even if it

does not split off at $T = 0$. It is due to the fact that an impurity spin is harder to flip than a typical host spin and its magnetization decreases much more slowly than the average magnetization $\langle S^z \rangle$ and as a result d_c decreases with the increase of temperature.

(ii) For $\alpha < 0$, we observe that even if the usual condition for a localized mode $d_c > 0$ is not satisfied, an excitation may split off the spin wave band, provided the magnetitude of the biquadratic parameter exceeds a certain critical value. It implies that in the case of a magnetic system which has a negative biquadratic exchange the localized modes may be observed at very low temperatures even if $d_c < 0$ at such temperatures. We conclude, therefore, that a negative biquadratic exchange enhances the possibilty of formation of a localized mode. This general behaviour is demonstrated in figure 1. If $|\alpha|$ is less than α_c, the localized mode may also be observed at some higher temperature which is, however, lower than the temperature at which a localized mode ought to be observed in absence of biquadratic exchange.

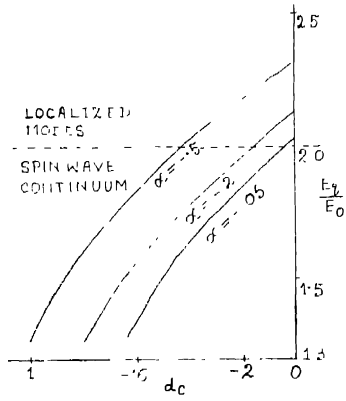

Fig. 1. Localized modes in a spin-1 lattice. Variation of E_q with d_c for various values of biquadratic parameter. Here α has been considered as positive.

(iii) For $\alpha > 0$, the situations become largely dependent on spin value since the third term in the expression for ϕ is related to S. This term may be of such magnitude that even if $d_c > 0$, no localized mode can be observed for a positive value of α. This implies that a positive biquadratic exchange, in some cases, hinders the formation of a localized mode; that is, in the system in which a localized mode should be observed at low temperatures (due to the condition $d_c > 0$), it is not actually observed upto certain high temperature. The situation is

demonstrated in figure 2. It is, indeed, evident directly from eq. (22) that for spin-$\frac{1}{2}$ case, the spin-dependent term of ϕ disappears and as a result one finds that the formation of a localized mode is always hindered. For all other spins, the situations become dependent on the magnitude of α and on the value of S.

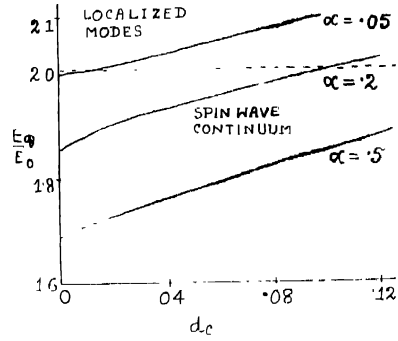

Fig. 2. Localized modes in a spin-1 lattice: Variation of E_q with d_c for various negative values of α.

It is necessary to discuss these observations with reference to some experimental results. We describe two well-known situations occurring in the resonance measurements of spin wave modes in $KMnF_3 : Mn^{++}$ and $Fe : Mn^{++}$. These situations are consistent, at least qualitatively, with the results obtained above. In order to examine the consistency of these results, it is, however, necessary to construct the rule for deciding the sign of the biquadratic parameter for a magnetic system.

5. Sign-Rule for Biquadratic Exchange

Several authors (Harris & Owen 1963, Rodbell *et al* 1964, Joseph 1965, Castets & Nauciel-Bloch 1972) have suggested the values of α for some magnetic systems by fitting their theories with the available experimental data. The general conclusion which has been reached from these observations is that both positive and negative values of α may be required for the interpretation of observed data. Purpose of this section is to construct a sign-rule for α from these observations.

In order to construct such rule (if it exists) we first examine the nature of the magnetization curves and their qualitative changes with respect to the variation of α. Brown (1971) carried out a qualitative study of the magnetization curves for $\alpha = 0$ and $\alpha = 1$ on the basis of molecular field theory (MFT). Similar curves may be investigated by using the Green's function theory (GFT). But

the GFT curves essentially depend on the form of the decoupling schemes utilized for reducing the equation of motion. Moreover we have to compare the magnetization curves for $\alpha \neq 0$ and those for $\alpha = 0$ and the results in both cases should be same.

The MFT curves of Brown for $\alpha = 0$ and $\alpha = 1$ are shown in Figure 1. These curves correspond to the spin-1 *bcc* lattice. It is to be noted from the figure that the curve for $\alpha = 1$ lies above the curve for $\alpha = 0$. For the sake of simplicity of presentation we call the curve for $\alpha = 0$ as a bilinear (BL) curve now instead of $\alpha = 0$ if one considers any positive value of α, the magnetization curve corresponding to this must lie above the BL curve and this is true for all spins and for all lattice structures. Brown (1971), however did not examine the nature of the magnetization curves for negative α. The magnetization curves for negative biquadratic parameter will lie below the BL curve if one adopts the MFT calculation. For negative α, one may, however, argue that the groundstate may not be ferromagnetic, since for a ferromagnetic groundstate one should have $J > 0$, $\alpha > 0$. But such argument is incorrect. The quantum condition for a ferromagnetic groundstate has been derived by Nauciel-Bloch *et al* (1972) which is $J > 0$, $-0{\cdot}5 < \alpha < 1$. It is to be mentioned that for any real ferromagnetic system α may not lie beyond this range.

If one attempts to examine the experimental magnetization curves, one naturally finds that these curves do not agree with the BL curve and that these will lie either above or below the BL curve. In corroboration with the observations of the previous paragraph, we therefore suggest the following rule for deciding the sign of the biquadratic parameter for a particular magnetic system: If the experimental magnetization curve for a magnetic system lies above the BL curve, the system should have a positive α and if below, a negative α.

It is necessary to test the validity of this rule with reference to previously determined values of p for several magnetic systems. Two such examples may be cited from the literature. One of these is the ferromagnetic sulphospinel $MnCr_2S_4$ which provides a good support of the rule. The comparison of the magnetization curves with the MFT result has been made by Nauciel-Bloch *et al* (1972). It will be found that the experimental magnetization curve lies below the BL curve and hence $MnCr_2S_4$ should have a negative biquadratic exchange and it is actually the case as observed by Castets & Nauciel-Bloch (1972). They showed that the experimental results could be explained satisfactorily if α would have been chosen a value $-0{\cdot}012$. Another example is $KMnF_3$ which has been found by Joseph (1965) to possess a negative α and it is also found that the experimental magnetization curve lies below the BL curve (Watarai & Kawasaki 1972). There should exist several other examples which may be believed to follow this rule.

The purpose of constructing this rule is that we have selected Fe and $KMnF_3$ for our discussion regarding the existince of localized modes and we do not know the sign of α for Fe, although it is known for $KMnF_3$. In addition to this, if one wishes to study the localized modes in some other magnetic substance which has not been studied experimentally, then by applying this sign-rule we can first decide the sign of α and then we may collect information regarding the temperature at which a localized mode may be observed This is, however, possible when the magnetization curve for that magnetic system is available If the magnetization curve is not available still then it is possible to obtain an estimate of the magnitude of α by a direct method It is known that the high-temperature series results provide an accurate description of magnetic properties Rushbrooke & Wood (1969) derived the expression for Curie temperature and susceptibility for ferromagnetic lattices using high-temperature series approximation Comparing these expressions with the corresponding expressions from the *bilinear+biquadratic* Hamiltonian using Green's functions, one can obtain the value of α in straight-forward manner The values of α for some typical magnetic systems have been calculated in this way and it is found that the sign of α in these cases agree exactly with the above rule Following this method we have calculated the value of α for $KNiF_3$

Before going to the discussion of the localized modes in two magnetic systems we have chosen for verification of the results of the present paper, it is necessary to apply the above stated rule to Fe We find that the experimental magnetiza-

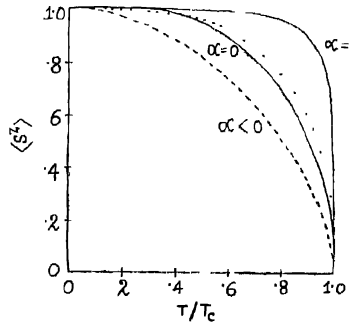

Fig. 3. Magnetization curves for a spin-1 lattice. Unbroken curves correesponds to molecular field calculations of Brown (1971) for $\alpha = 0$ and $\alpha = 1$. Broken curve represents the case of $\alpha < 0$. The dots represent the experimental values of iron (Callen *et al* 1965).

tion curve for Fe is available and it is shown in figure 3. It is to be noticed that this curve lies above the BL curve (Callen 1965) Hence according to the signrule, the sign of α is positive.

6. Localized Modes in $KMnF_3 : Ni^{++}$ and $Fe : Mn^{++}$

The results obtained in Sec 4, along with the sign-rule of p discussed in the preceding section may now be employed to explain, at least qualitatively, the appearance of localized spin wave modes in $KMnF_3$ and Fe doped by impurities Ni and Mn respectively In $KMnF_3$ Ni^{++} since the host spin $S = 5/2$ and the impurity spin $S_I = 1$, one has $d_c < 0$ at very low temperatures, and hence no localized mode ought to be observed upto a certain high temperature, but such a mode has actually been reported by Johnson *et al* (1966) at very low temperature (at about 4·2°K) in spite of the fact that at such a low temperature d_c is still less than zero It has been found that a negative p causes a localized excitation to split off from the spin wave continuum even if d_c is less than zero at such a low temperature (Fig 1) Therefore, the experimental situation occurring in $KMnF_3 : Ni^{++}$ is consistent with the theoretical results obtained in the present paper In addition to this, we may establish the validity of the results quantitatively with some reasonable accuracy We find that at $T = 0$°K, d_c is equal to −0·6 and as temperature increases, this value of d_c increases At about 4·2°K, one can show from the data presented by Watarai & Kawasaki (1972) that $d_c = -0{\cdot}4$ Considering this value we get from eq. (21) the conclusion that a localized mode can be observed if one chooses α to be equal to − 0·08 which may be compared with the value obtained by Joseph (1965) This value is although much lower than that of Joseph (1965), yet the qualitative results regarding the earlier occurrence (that means at low temperatures) of the localized modes in $KMnF_3$ is interesting and is definitely helpful to any further experimental work on any new magnetic system doped by impurities The deviation of the value calculated above is due to the Anderson-Callen decoupling scheme which has not been found to be accurate so far as the groundstate is concerned although this decoupling scheme gives good results at high temperatures (Chakraborty 1976)

We now test the consistency of the result (iii) mentioned in Sec 4 with reference to the NMR measurements in Fe in presence of Mn as impurities In this case since $S = 1$ and $S_I = 3/2$, a localized mode ought to be observed at low temperatures but actually the experimental results show that in Fe Mn^{++} a localized mode does appear at much high temperature (Jaccarino *et al* 1964) Thus although $d_c < 0$ at low temperatures the formation of localized modes is hindered. This is consistent with the result obtained in the present paper For Fe, α is positive and so the formation of a localized mode should always be hindered

7. Predicted Behaviour of $KNiF_3 : Mn^{++}$

The magnetic structure of $KNiF_3$ has been determined by neutron-diffraction techniques (Scatturin *et al* 1961) It is found that $KNiF_3$ is a cubic

Perkoskite and Lines (1967) pointed out that its magnetic properties are describable, to a good approximation, in terms of an isotropic spin-Hamiltonian with $S = 1$. The Neel temperature of this Pervoskite has been measured by Hirakawa *et al* (1960) and was recorded to be 253°K. It should be remarked that a simple bilinear exchange of Heisenberg type is not able to reproduce the results accurately and we will find that the biquadratic exchange has a significant effect on the magnetic properties. We shall show first the necessity of including a biquadratic exchange in $KNiF_3$.

High-temperature series calculation of Rushbrooke & Wood (1969) gives accurate value for Curie temperature which for a simple nearest-neighbour exchange Heisenberg system is represented by

$$-\frac{k_B T_c}{J} = \frac{5(z-1)}{192}\{11S(S+1)-1\} \qquad \ldots (23)$$

with a similar expression for Neel temperature.

We compare this expression with that obtained for a spin Hamiltonian which includes both bilinear and biquadratic interactions. Various thermodynamics properties have been discussed elsewhere. We only quote here the transition temperature for such a system. By means of the decoupling schemes utilized in the present paper one may obtain the following expression for Curie temperature

$$\frac{k_B T_c}{zJ} = \frac{4}{3F_1}(1-\alpha/2) \qquad \ldots (24)$$

where the symbol F_1 is the usual Watson sum given by

$$F_1 = (1/N)\Sigma_k(1-\gamma_k)^{-1}$$

$$\gamma_k = \frac{J(k)}{J(0)} = \sum_\delta \exp(i\boldsymbol{k}.\boldsymbol{\delta})$$

$\boldsymbol{\delta}$ being a nearest-neighbour vector. It should be pointed out that an exactly similar expression for Neel temperature can be obtained. It is also necessary to mention that in deriving eq. (24) we have utilized RPA for those Green's functions which occur in the bilinear part of the equation of motion.

Comparing eqs (23) and (24) one obtains the result which is found to yield the Neel temperature accurately. Taking $J = 93$°K we obtain from eq. (24) $T_N = 250$°K which is remarkably close to the experimental value $T_N = 253$°K.

We thus find that α for $KNiF_3$ is positive and hence the occurrence of localized modes is hindered in spite of the fact that in $KNiF_3$. Mn^{++} one has $S = 1$, $S_I = 3/2$. If the presence of biquadratic exchange is not accounted, a localized mode should be observed at low temperatures. Since a positive biquadratic

exchange is present in the host system, the appearance of localized mode is hindered and it will be observed at high temperatures A rough estimate of this temperature can be readily obtained It is known that the impurity magnetization may be accurately determined by the following expression (Callen *et al* 1965)

$$<S_c^z> = B(<S^z>/\tau), \quad \tau = \frac{k_B T}{J}$$

where B is the Brillouin function corresponding to the spin S, $<S>$ is the host-magnetization We have chosen λ equal to unity Utilizing this relationship one finds that a localized mode should be observed at about 157°K Below this temperature no localized mode can be observed. Such a high temperature is evidently due to the large value of biquadratic parameter

8 Concluding Remarks

Using the Green's function formalism the effect of biquadratic exchange on the localized spin wave modes has been studied It seems necessary to remark that the localized mode as discussed in previous sections is an s_0 mode since we have assumed in the biginning that the effect of perturbation due to the presence of impurity is highly localized at the impurity site c The effect of biquadratic exchange on p and d modes may be significant and such problem is to be discussed by using more sophisticated methods It is also important to mention that the nature of the localized spin wave states in a biquadratic-exchange ferromagnet is an aspect which should be investigated by using the normalized impurity wave function of Tonegawa (1972) In the case of an anisotropic-exchange-ferromagnetic it has been found that (Tanaka 1973) the spin wave spectrum has an energy gap which is proportional to the anisotropy Similarly in the present case one should also expect an energy gap proportional to the strength of the biquadratic exchange Detail investigations in this regard are necessary. There remains also another two aspects which should be considered along with these : (1) In writing out the starting Hamiltonian we have assumed at the beginning that I'_{ic} and I'_{ic} are small. In reality, however, I_{ic} is not very small although it is much smaller than J_{ic} The assumption that $I'_{ic} \simeq 0$ is not, however, unrealistic, so far as the magnetic of J'_{ic} is concerned It is observed that $J' \sim 10^{-2} J - 10^{-1} J$ and $I \sim 10^{-1} J$ It is likewise expected that $I' \sim 10^{-2} J'$ or less than this Therefore, $I' \sim 10^{-4} J$ and hence it can be ignored The problem of inclusion of I_{ic} will be considered in future publication (2) It is necessary to point out the internal consistency in the treatment presented here regarding the biquadratic term In dealing with the biquadratic term *vis a vis* the bilinear term one should consider the second order correction due to the latter along with the first order correction due to the former In the present treatment we have considered only the first order correction due to both

the terms The consideration of the second order correction due to the bilinear term is mathematically more complex and such problem cannot be easily solved

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